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(Invited) In Situ TEM Study of Reduction and Reoxidation of NiO and NiO-YSZ Composites

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Nickel-yttria-stabilised zirconia (YSZ) solid oxide fuel cell (SOFC) anodes exhibit a dimensional instability when experiencing a reduction-oxidation cycle. As fuel is supplied on the anode side, as-sintered NiO reduces to metallic Ni and remains in this state during operation; yet several factors may lead to an accidental reoxidation of the Ni, which may rupture parts of the cell, hence degrading its performance.

The mechanisms behind the dimensional instability of Ni(-YSZ) anodes were investigated through environmental transmission electron microscopy. NiO particles and NiO/YSZ composites were reduced and reoxidised in the microscope in a few mbar of H₂ and O₂, respectively, up to 500-850°C. Images, diffraction patterns, electron energy-loss spectra (EELS) and energy-filtered micrographs (EFTEM) were acquired to capture in situ the nanostructure, crystallography and chemistry. Reaction kinetics were retrieved from both the changes in shapes of the Ni L_{2,3} edges in energy-loss spectra and from energy-filtered images (with nm-resolution), to provide quantitative data, which were correlated to the nanostructure.

Figure – (a) as-sintered NiO particles observed (b) after reduction (at 600°C during 210 min in 1.3 mbar of H₂) and (c) after reoxidation (at 600°C) after heating from 250°C at a rate of 4°C/min in 3.2 mbar of O₂). In (d), the projected areas of (a–c) are superimposed to the image shown in (c). Reduction results in a shrinkage of the projected area of -15% between (a) and (b) in the region of interest circled in (d), while oxidation induces an expansion of the projected area of +65% between (b) and (c). The projected area of NiO expands by +40% between (a) and (c) after one redox cycle.

While the surface nucleation of Ni domains, their growth and impingement control the reduction of NiO particles (Avrami-type mechanism), the results revealed a modification of the mechanisms in the presence of YSZ, with the transfer of oxygen from NiO to the oxygen vacancies of YSZ triggering the reaction, before free surface reduction starts. Intragranular voids formed in both cases as oxygen is removed. The final Ni structure at high temperature was then observed to coarsen as it minimises its surface energy, with the percolation of the Ni phase influenced by the symmetry of its grain boundaries. The reoxidation of Ni is controlled mainly by the outward diffusion of Ni ions through the grain boundaries of the growing NiO film, rather than by a Ni/NiO or NiO/O₂ interfacial reaction limitation. While some NiO inward growth occurred through the formation of oxide film cracks, the Ni²⁺ outward diffusion process remains unbalanced and voids form in the NiO phase. These internal voids are responsible for the dimensional instability of the composite along with Ni coarsening at high temperature. Several parameters for improved performance and redox tolerance are identified based on these results.

Complementary data included post-exposure microscopy, in situ X-ray diffraction and density functional theory computations. With the complementary XRD results and analyses done on larger sample volumes, larger H₂ gas flow and pressure than in the E-TEM conditions, it was shown that the reduction reaction in the ETEM is intrinsic, up to a conversion plateau of 60%, after which it is limited by too slow evacuation of the steam produced by the reduction reaction itself. Scanning TEM (STEM) with elemental analysis (EDX) was employed for trace impurity detection in NiO-YSZ structures, both for as sintered and exposed samples, showing the segregation of impurities (mainly Al and Si) at Ni-Ni interfaces in the form of a glassy film supporting Ni nanoparticles. Some of these impurities were unexpected and could affect the anode performance during operation.

Figure 1

